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A Study on Mathematical Models for Predicting Water Activity in Multicomponent Foods

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Abstract : A model to predict water activity (equilibrium relative humidity/100) in multicomponent food mixtures is developed. It is based on balancing masses of water and dry matter and assumes that no interactions affecting water activity of the ingredients occur during mixing. Explicit solutions are presented for the linear and Smith forms of the isotherm equations. A numerical procedure is used to calculate the water activity for nonlinear isotherm equations. An example using data fro m the literature illustrates very good fittings by using appropriate isotherm equation for calculating of water activity of the mixture.

Introduction

A frequent operation in the development of food products is the mixing of different ingredients to produce a composite food. When these ingredients are mixed and sealed perfectly, they will reach a final equilibrium state by a change in moisture. The driving force is due to the difference in the vapor pressures of the ingredients.

Because of the importance of water activity (equilibrium relative humidity/100) on the storage properties of foods, such as hardness, storage period, and crispness, it is often necessary to know the final water activity (A_w) of the mixture. Several equations that predict the water activity of the final equilibrium state of the composite food have been proposed. Salwin and Slawson (1959) assumed the sorption isotherms of foods exhibited a linear relationship between A_w and moisture content. They gave an equation for predicting water activity based on the initial A_w value, weights, and parameters of the linear line for each ingredient. Unfortunately, the linear relation was not valid in the low and high ranges of water activity.

Lang and Steinberg (1980) attempted to show the validity for the hypothesis that at a given A_w the moisture content of a mixture was equal to a weighted average of the moisture content of each component at that A_w. They concluded that each compon-

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ent absorbed water independently of the others. Similar research by Iglesias et al. (1980) found that the interactions between components definitely altered the individual sorption properties, leading to significant differences between predicted and measured values.

Using the equation presented by Smith (1947) instead of the linearized isotherm, La ng and Steinberg (1981) proposed a new equation to predict the final water activity by knowing the weight and parameters of the Smith equation for each component and the moisture content of mixture. The applicable range of A_w for this equation is from 0.30 to 0.95.

The linear and Smith isotherm sorption equations are only valid in a limited range and have only been fit for particular food products. Therefore, a general model for predicting Aw with the best "fitting-agreement" equation for each ingredient over the applicable range would be useful.

Model Development

The assumption for this model is that there is no moisture loss or gain in the system during the mixing process. To ensure the validity of the A_w prediicton, the model also requires no direct interactions between the ingredients of the mixture.

From the concept of a mass balance, the total quantity of water within the mixture is equal to the sum of the water that exists in each ingredient and can be expressed as

$$W_t * M_t = \sum_{i=1}^{n} W_i * M_i \quad \cdots\cdots (1)$$

where: M_i = moisture content of ingredient i, decimal dry basis
M_t = moisture content of mixture, decimal dry basis
W_i = dry matter of ingredient i, g
W_t = total dry matter, g
n = number of ingredients in mixture

Assuming no moisture loss during the mixing process, then,

$$W_t * M_t = \sum_{i=1}^{n} W_i * M_i(\text{initial stage}) = \sum_{i=1}^{n} W_i * M_i(\text{final stage}) \quad \cdots\cdots (2)$$

Under constant temperature, the moisture content of foods can be expressed as a function of water activity.

$$M = f(A_w) \quad \cdots\cdots (3)$$

Therefore,

$$W_t * M_t = \sum_{i=1}^{n} W_i * f_i(A_{wi}) = \sum_{i=1}^{n} W_i * f_i(A_{weq}) \quad \cdots\cdots (4)$$

where: A_{wi} = initial A_w of ingredient i, decimal
A_{weq} = equilibrium A_w of mixture, decimal
f_i = isotherm function for ingredient i

Any sorption equation can be substituted into Eq. (4) to solve the mixing problem. Since each food ingredient has its own characteristic "best fit" equation for its applicable range of A_w, Eq(4) can serve as the universal equation for the mixing operation.

The linear equation and Smith equation have a linear form for moisture content. Eq (4) can be further simplified in these cases.

Linear Isotherm Equation

$$M = b * A_w + c \quad \cdots\cdots (5)$$

Substituting into Eq (4) yields

$$W_t * M_t = \sum_{i=1}^{n} W_i * f(A_{wi}) = \sum_{i=1}^{n} W_i * (b_i * A_{wi} + c_i) \quad \cdots\cdots (6)$$

$$W_t * M_t = \sum_{i=1}^{n} W_i * f(A_{weq}) = \sum_{i=1}^{n} W_i * (b_i * A_{weq} + c_i) \quad \cdots\cdots (7)$$

Combining Eq (6) and Eq (7) and solving for A_{weq} yields

$$A_{weq} = \frac{\sum_{i=1}^{n} W_i * b_i * A_{wi}}{\sum_{i=1}^{n} W_i * b_i} \quad \cdots\cdots (8)$$

Eq (8) is the model developed by Salwin and Slawson (1959). When the moisture content of the mixture is known, Eqs. (6) and (8) can be combined into the form.

$$A_{weq} = \frac{W_t * M_t - \sum_{i=1}^{n} W_i * c_i}{\sum_{i=1}^{n} W_i * b_i} \quad \cdots\cdots (9)$$

Smith Isotherm Equations

In the Smith equation, M and In $(1-A_w)$ have a linear relation:

$$M = a + b * \ln(1 - A_w) \quad \cdots\cdots (10)$$

Substituting Eq (10) into (4) yields

$$W_t * M_t = \sum_{i=1}^{n} W_i * f(A_{wi}) = \sum_{i=1}^{n} W_i * (a_i + b_i * \ln (1 - A_{wi})) \quad \cdots\cdots (11)$$

$$W_t * M_t = \sum_{i=1}^{n} W_i * f(A_{weq}) = \sum_{i=1}^{n} W_i * (a_i + b_i * \ln (1 - A_{weq})) \quad \cdots\cdots (12)$$

Therefore,

$$\ln(1 - A_{weq}) = \frac{\sum_{i=1}^{n} W_i * b_i * \ln(1 - A_i)}{\sum_{i=1}^{n} W_i * b_i} \quad \cdots\cdots (13)$$

When the moisture content of the mixture is known, combining Eqs (11) and (13) results in:

$$\ln(1-A_{weq}) = \frac{W_t * M_t - \sum_{i=1}^{n} W_i * a_i}{\sum_{i=1}^{n} W_i * b_i} \quad \cdots\cdots (14)$$

This is the equation proposed by Lang and Steinberg (1981).

Nonlinear Isotherm Equations

Several common sorption equations have nonlinear forms. These include equations presented by Henderson (1952), Chung and Pfost (1967), Halsey (1947), Halsey (1948), Oswin (1946), and Brunauer et al. (1938).

Because no linear relation exists between the moisture content and A_w (or the transformed A_w), these equations cannot be simplified as can the linear and Smith equations. Therefore, an explicit expression for the A_w of the mixture cannot be found. However, the solution can be found by numerical methods. A simple iterative scheme can provide a convenient and rapid way of predicting the final A_w value for the mixture.

There are three methods to obtain the roots of a nonlinear equation. Due to the curvature of the sorption isotherm, divergence could occur for the Newton and secant methods in the inflection region. Also, the Newton method involves a complex form of the first derivative for the sorption equation. The bisection method provides a good method to obtain the solution (Atkinson, 1985).

Application of Model

The mixing of dried egg albumen and soy protein was selected as the example to predict the water activity of the mixture. These data are adopted from Bone (1987).

The nonlinear isotherm equation chosen to fit the data is the one presentede by Oswin (1946). The equation is,

$$M = b * \left(\frac{A_w}{1-A_w}\right)^c \quad \cdots\cdots (15)$$

where: b and c are product parameters.

For egg albumen, the Oswin equation becomes,

$$M = 11.711 \left(\frac{A_w}{1-A_w}\right)^{0.60496} \quad \cdots\cdots (16)$$

The linear sorption equation for this product is,

$$M = -16.063 + 56.276 * A_w \quad \cdots\cdots (17)$$

For soy protein, the Oswin equation becomes,

$$M = 10.010 \left(\frac{A_w}{1-A_w}\right)^{0.53050} \quad \cdots\cdots (18)$$

The linear equation is,

$$M = -10.105 + 41.896 * A_w \quad \cdots\cdots (19)$$

The isotherm data at 25°C for both ingredients and the Oswin equations (16 and 18) fit to the data are plotted in Figure 1. The equations closely fit the data.

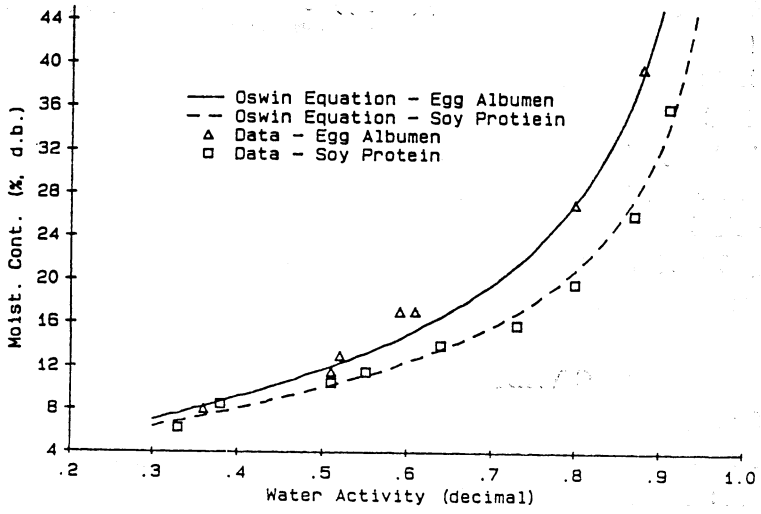

Figure 1. Adsorption isotherms at 25°C, for dried egg albumen and soy protein (data from Bone, 1987).

A 50 : 50 blend of dried egg albumen and soy protein was used to compare the validity of the prediction for the mixing model.

Combining Eq. (4) and the two isotherm equations, the predicted isotherm relation for the mixture for the linear equation is,

$$M_t = -13.084 + 49.086 * A_w \quad \cdots\cdots (20)$$

and for the Oswin equation is,

$$M_t = 5.0051 * \left(\frac{A_w}{1-A_w}\right)^{0.53050} + 5.8555 * \left(\frac{A_w}{1-A_w}\right)^{0.60496} \quad \cdots\cdots (21)$$

The A_w value for each M_t can be solved by Eq (20) or (21). A program written in BASIC that solved Eq (21), a nonlinear equation, is shown in the Figure 2. Other nonlinear equations can also be solved with this program. For mixing conditions, the user needs ony to substitute the new equation in the program at line 30.

The actual A_w values and the predicted values from the two sorption equations (20 and 21) are shown in Fig. 3. The Oswin equation provides good results, especially for an A_w of 0.6 to 0.75 which is the range where development of fungi starts. Large deviations are found for the results of the linear equation. This prediction would give incorrect information about safe storage of food products. For example, the actualaA$_w$ for the mixture of 18% m. c. is nearly 0.7, a critical level for fungi development. However, the linear equation predicts a value for A_w of 0.62 which appears to be relatively safe. These results show the importantance of using an appropriately shaped isotherm equation when evaluating mixing problems.

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10 REM: SOLVE NONLINEAR EQUATION BY BISECTION METHOD
20 INPUT "MT=?"; MT
30 DEF FNE(X)=MT-5.0051*(X/(1-X))^0.53050-5.8555*(X/(1-X))^0.60496
40 REM
50 A=0.01 : B=0.99 : C=0.5
55 D=B-C
60 IF ABS (D)<1.0E-5 GOTO 150
70 PB=FNF (B) : PC=FNF (C)
80 J=PB*PC
90 IF J>0 GOTO 110
100 A=C : GOTO 130
110 B=C
120 REM: UPDATA C VALUE
130 C=(A+B)/2
140 GOTO 55
150 PRINT: PRINT "AW=" ; C
209 END
```

Figure 2. BASIC program to solve a nonlinear equation by the bisection method-example equation defined in line 30.

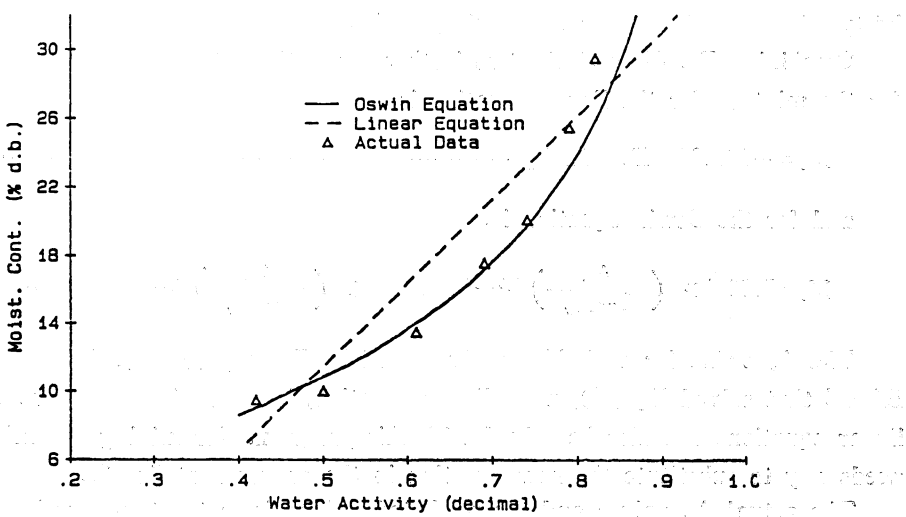

Figure 3. Predicted and actual isotherms at 25°C for 50 : 50 mix of egg albumen and soy protein (data from Bone, 1987).

Summary and Conclusions

The relationship of water activity for multicomponent foods to the components making up the mixture is developed using a mass balance principle. Because of the limited A_w range for the application of the linear and Smith isotherm equations, nonlinear sorption equations provide a better fit for sorption data. A numerical procedure

using the bisection method to solve nonlinear equation isotherm was developed. An example mixing problem showed that a nonlinear isotherm equation provided better prediction of water activity than a linear eqvation.

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多成份食品水活性之預測模式

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摘 要

食品水活性的性質在混合、貯存、運輸等加工作業上十分之重要。此研究之目的即在於推導與驗證由多種成份混合製成食品的水活性預測模式。其應用之假設條件爲食品乾物質與所含水份的總質量不變，且在混合過程中無化學反應發生。利用等溫水份線的直線公式和史密斯公式，雖然可以直接求得預測值，但誤差偏大。利用非線性公式推衍所得的混合模式可以以數值方法求得預測值，其驗證結果則十分精確。

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